

WHAT IS CLAIMED IS:

1. A method of minimizing the production of one or more phosphonium ion ligand degradation products in a reaction process wherein a polyunsaturated olefin is reacted in the presence of a transition metal-triorganophosphine ligand complex catalyst to form as a product, by-product, or intermediate product a conjugated functionalized olefin having a carbon-carbon double bond conjugated to an α -electron-withdrawing group, the minimization method comprising (a) conducting the reaction process with a triorganophosphine ligand having a steric or electronic property, or a combination thereof, sufficient to minimize the formation of phosphonium ion ligand degradation product(s); or (b) conducting the reaction process to a polyunsaturated olefin conversion, at a temperature, at a pressure, or at a combination of said process conditions sufficient to minimize the formation of phosphonium ion ligand degradation product(s); or (c) conducting the process by combining a method of (a) with a method of (b).

2. The method of Claim 1 wherein the steric property is estimated by ligand cone angle, and the triorganophosphine has a ligand cone angle greater than about 135°.

3. The method of Claim 1 wherein the electronic property is measured by pKa, and the triorganophosphine ligand has a pKa of less than about 8.3.

4. The method of Claim 1 wherein the polyunsaturated olefin conversion is greater than about 80 weight percent and less than about 95 weight percent.

5. The method of Claim 1 wherein the reaction temperature is greater than about 45°C and less than about 95°C.

6. The method of Claim 1 wherein the total pressure is greater than about 300 psig and less than about 5,000 psig.

7. The method of Claim 1 wherein the triorganophosphine ligand is selected from tri-isopropylphosphine, tri-isobutylphosphine, tri-*t*-butylphosphine, tricyclohexylphosphine, cyclohexyldi-*n*-butylphosphine, tri(*o*-methylphenyl)-phosphine, tri-*n*-butylphosphine, tri-*n*-octylphosphine, dimethylphenylphosphine,

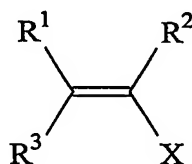
methyldiphenylphosphine, and triphenylphosphine, the sulfonated salts of the aforementioned ligands, and any combination of mixtures thereof.

8. The method of Claim 1 wherein the polyunsaturated olefin is a C₄₋₆₀ polyene.

9. The method of Claim 8 wherein the C₄₋₆₀ polyene is selected from the group consisting of butadiene, pentadienes, hexadienes, heptadienes, octadienes, dicyclopentadiene, hexatrienes, octatrienes, cyclooctadiene, 2,4-pentadienoic acid, 2,4-hexadienoic acid (sorbic), 2,4-decadienoic acid, 2,4-dodecadienoic acid, *cis*-9,*cis*-12-octadecadienoic acid (linoleic), *trans*-9,*trans*-12-octadecadienoic acid (linolelaidic), 5,6-octadecadienoic acid (laballenic), 5,13-docosadienoic acid, 6,10,14-hexadecatrienoic acid (hiragonic), *cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid (linolenic), *cis*-9,*trans*-11,*trans*-13-octadecatrienoic acid (α -eleostearic), *trans*-9,*trans*-11,*trans*-13-octadecatrienoic acid (β -eleostearic), and the mono, di, and tri-glycerol esters and C₁₋₈ alkyl esters of the aforementioned carboxylic acids.

10. The method of Claim 1 wherein the α -electron-withdrawing group is selected from aldehyde, ketone, ester, acid, and nitrile functionalities.

11. The method of Claim 1 wherein the conjugated functionalized olefin is represented by the formula:



wherein X is selected from the group consisting of formyl, keto, ester, acid, and nitrile; and wherein each R¹, R², and R³ is independently selected from hydrogen and C₁₋₆₀ monovalent hydrocarbon radicals, with the proviso that at least one of R¹, R², or R³ is a monovalent hydrocarbon radical.

12. The method of Claim 1 wherein the reaction process comprises hydroformylation, hydroacylation, hydroesterification, carbonylation, or hydrocyanation.

13. The method of Claim 1 wherein the rate of ligand usage is less than about 2 grams ligand per liter reaction fluid per day.

14. The method of Claim 1 wherein the rate of ligand usage is less than about 0.1 gram ligand per liter reaction fluid per day.

5 15. The method of Claim 1 wherein the reaction process comprises contacting a C₄₋₆₀ polyunsaturated olefin with carbon monoxide, optionally in the presence hydrogen, water, or alcohol, to form as a product, by-product, or intermediate product an α,β -unsaturated aldehyde, ketone, ester, or acid.

10 16. The method of Claim 15 wherein the minimization method comprises (a) conducting the carbonylation reaction in the presence of a triorganophosphine ligand having a cone angle greater than about 135°, or a pKa less than about 8.3, or a combination thereof; or (b) conducting the carbonylation process to a polyunsaturated olefin conversion greater than about 80 weight percent and less than about 95 weight percent, or at a temperature greater than about 45°C and less
15 than about 95°C, or at a pressure greater than about 300 psig and less than about 5,000 psig, or at a combination of said process conditions; or (c) conducting the process by combining a method of (a) with a method of (b).

17. The method of Claim 1 wherein the reaction process comprises contacting a polyunsaturated olefin with hydrogen cyanide under conditions sufficient
20 to form as a product, by-product, or intermediate product an α,β -unsaturated nitrile.

18. The method of Claim 17 wherein the polyunsaturated olefin comprises a C₄₋₆₀ polyene; and the minimization method comprises (a) conducting the hydrocyanation process in the presence of a triorganophosphine ligand having a cone angle greater than about 135°, or a pKa less than about 8.3, or a combination thereof;
25 or (b) conducting the hydrocyanation process to a polyene conversion greater than about 80 weight percent and less than about 95 weight percent, or at a temperature greater than about 45°C and less than about 95°C, or at a pressure greater than about 300 psig and less than about 5,000 psig, or at a combination of aforementioned process conditions; or (c) conducting the process by combining a method of (a) with a
30 method of (b).

19. A process of minimizing the formation of one or more phosphonium ion ligand degradation products in a reaction process wherein an unconjugated functionalized olefin, characterized as having at least one carbon-carbon double bond in unconjugated position relative to an α -electron-withdrawing group selected from formyl, keto, ester, acid, and nitrile functionalities, is reacted in the presence of a transition metal-triorganophosphine ligand complex catalyst to form as a product, by-product, or intermediate product a conjugated functionalized olefin, characterized as having a carbon-carbon double bond conjugated to the α -electron-withdrawing group, the minimization method comprising (a) conducting the reaction process with a triorganophosphine ligand having a steric or electronic property, or combination thereof, sufficient to minimize the formation of phosphonium ion ligand degradation product(s); or (b) conducting the reaction process to a conversion of unconjugated functionalized olefin, or at a temperature, or at a pressure, or at a combination of said process conditions sufficient to minimize the formation of phosphonium ion ligand degradation product(s); or (c) conducting the reaction process by combining a method of (a) with a method of (b)

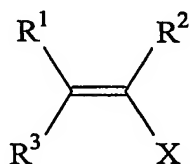
20. The process of Claim 19 wherein the process is conducted in the presence of a triorganophosphine ligand having a cone angle greater than about 135°, or a pKa less than about 8.3, or a combination thereof; or (b) wherein the process is conducted to a conversion of unconjugated functionalized olefin of greater than about 80 weight percent and less than about 95 weight percent, or at a temperature greater than about 45°C and less than about 95°C, or at a pressure greater than about 300 psig and less than about 5,000 psig, or at a combination of said process conditions; or (c) conducting the process by combining a method of (a) with a method of (b).

21. The process of Claim 19 wherein the unconjugated functionalized olefin is 3-pentenal or an unconjugated unsaturated fatty aldehyde, alcohol, or ester.

22. A process of reverting a phosphonium ion ligand degradation product or mixture of such products back to triorganophosphine ligand(s), the phosphonium ion ligand degradation product or mixture of such products being capable of reversion to useful triorganophosphine ligand, and comprising an adduct of a triorganophosphine ligand and a conjugated functionalized olefin having a carbon-

carbon double bond conjugated to an α -electron-withdrawing group; the reversion process comprising treating a reaction product fluid containing the phosphonium ion ligand degradation product or mixture of such products with an inert gas, hydrogen, synthesis gas, or a combination thereof, under conditions sufficient to revert the phosphonium ion ligand degradation product or mixture of such products back to triorganophosphine ligand or mixture of triorganophosphine ligands.

23. The process of Claim 22 wherein the conjugated functionalized olefin is represented by the formula:



wherein X is selected from the group consisting of formyl, keto, ester, acid, and nitrile; and wherein each R^1 , R^2 , and R^3 is independently selected from hydrogen and C_{1-60} monovalent hydrocarbon radicals, with the proviso that at least one of R^1 , R^2 , or R^3 is a monovalent hydrocarbon radical.

24. The process of Claim 22 wherein the conjugated functionalized olefin is a C_{5-60} α,β -unsaturated aldehyde, ketone, ester, acid, or nitrile.

25. The process of Claim 22 wherein the conjugated functionalized olefin is 2-pentenal or an unsaturated fatty aldehyde, alcohol, or ester.

26. The process of Claim 22 wherein the triorganophosphine ligand is selected from the group consisting of tri-isopropylphosphine, tri-isobutylphosphine, tri-t-butylphosphine, tri-n-octylphosphine, tricyclohexyl-phosphine, cyclohexyldi-n-butylphosphine, tri(*o*-methylphenyl)phosphine, cyclohexylphosphine, tri-n-butylphosphine, dimethylphenylphosphine, methyldiphenylphosphine, dicyclohexylphenylphosphine, triphenylphosphine, the sulfonated salts of the aforementioned phosphines, and any combination thereof.

27. The process of Claim 22 wherein the inert gas is selected from nitrogen, helium, argon, methane, carbon monoxide, steam, and mixtures thereof.

28. The process of Claim 22 wherein the synthesis gas CO/H₂ comprises a molar ratio from 10/1 to 1/10.

29. The process of Claim 22 wherein the reversion process is conducted at a temperature greater than about 50°C and less than about 150°C.

5 30. The process of Claim 22 wherein the phosphonium ion ligand degradation product comprises an adduct of a triorganophosphine ligand and 2-pentenal; and the reaction product fluid is treated with an inert gas selected from nitrogen, helium, argon, carbon monoxide, methane, and steam, under conditions sufficient to volatilize 2-pentenal and cause reversion of the ligand degradation
10 product back to triorganophosphine ligand.

31. The process of Claim 22 wherein the ligand degradation product comprises an adduct of a triorganophosphine ligand and 2-pentenal; and the reaction product fluid is treated with a source of hydrogen under conditions sufficient to hydrogenate 2-pentenal to pentanal and/or pentanol, thereby reverting the
15 phosphonium ion ligand degradation product back to triorganophosphine ligand.

32. The process of Claim 22 wherein the ligand degradation product comprises an adduct of a triorganophosphine ligand and 2-pentenal; and the reaction product fluid is treated with a source of synthesis gas under conditions sufficient to hydroformylate 2-pentenal, thereby reverting the phosphonium ion ligand degradation
20 product back to triorganophosphine ligand.

33. An integrated process for carbonylation of a polyunsaturated olefin or mixture thereof comprising (a) contacting a polyunsaturated olefin or mixture thereof with carbon monoxide, optionally, in the presence of hydrogen, alcohol or water, and in the presence of a transition metal-triorganophosphine ligand complex catalyst and free
25 triorganophosphine ligand, under process conditions sufficient to prepare a reaction product fluid comprising a transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine ligand, one or more reaction products, by-products, and/or intermediate products including an α,β -unsaturated aldehyde, ketone, ester, or acid, and one or more phosphonium ion ligand degradation products capable of reversion to useful ligand;
30 (b) treating the reaction product fluid from step (a) with an inert gas, hydrogen, synthesis

gas, or a mixture thereof under conditions sufficient to revert the one or more phosphonium ion ligand degradation products back to triorganophosphine ligand; (c) feeding the reaction product fluid taken from step (b), now containing reduced amounts of phosphonium ion ligand degradation products, to a vaporizer or an extractor for separation into a first phase
5 containing reaction products, by-products, and/or intermediate products and a second phase containing transition metal-triorganophosphine ligand complex catalyst and optionally free triorganophosphine ligand; and (d) recycling the second phase from step (c) containing the transition metal-triorganophosphine ligand complex catalyst and optionally free triorganophosphine ligand back to reaction process step (a).

10 34. An integrated process for carbonylation of a polyunsaturated olefin or a mixture thereof comprising (a) contacting a polyunsaturated olefin or mixture thereof with carbon monoxide, optionally, in the presence of hydrogen, alcohol, or water, and in the presence of a transition metal-triorganophosphine ligand complex catalyst and free triorganophosphine ligand, under process conditions sufficient to prepare a reaction product
15 fluid comprising a transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine ligand, one or more reaction products, by-products, and/or intermediate products including an α,β -unsaturated aldehyde, ketone, ester, or acid, and one or more phosphonium ion ligand degradation products capable of reversion; (b) feeding the reaction product fluid from step (a) to a vaporizer or an extractor for separation into a first
20 phase containing reaction products, by-products, and/or intermediate products, and a second phase containing the transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine ligand, and one or more phosphonium ion ligand degradation products; (c) treating the second phase from step (b) containing the transition metal-triorganophosphine ligand complex catalyst, optionally free triorganophosphine
25 ligand, and phosphonium ion ligand degradation products with an inert gas, hydrogen, synthesis gas, or a mixture thereof under conditions sufficient to revert the phosphonium ion ligand degradation products back to triorganophosphine ligand; and (d) recycling the phase containing the transition metal-triorganophosphine ligand complex catalyst and optionally free triorganophosphine ligand, now containing reduced amounts of phosphonium ion
30 ligand degradation products, back to reaction process step (a).